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# Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and *N*-Methylaniline

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The rate of elimination of hydrogen from dimethylaluminum hydride and *N*-methylaniline has been measured at −63 °C in toluene solution. Reaction conditions include equal concentrations of dimethylaluminum hydride and the amine and pseudo-first-order conditions with excess amine. The kinetics data are consistent with a second-order rate law which is complicated by an equilibrium. The following steps of the mechanism determine the rate of elimination of hydrogen:

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \overset{K_a}{\rightleftharpoons} H(CH_3)_2AlN(C_6H_5)(CH_3)H$$

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3)$$

Our results are consistent with the conclusion that adduct formation is a "dead-end" path for the elimination reaction. The elimination reaction is not a reaction of a preformed adduct. The factors responsible for the formation of only a dimeric aluminum–nitrogen product, $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, and the predominance of the cis isomer over the trans isomer (80/20%) are discussed. A ${}_{2}\pi_{s} + {}_{2}\pi_{a}$ cycloaddition reaction which minimizes interactions between the bulky phenyl groups is proposed.

## Introduction

The cleavage of metal–carbon bonds by protic acids is a process fundamental to organometallic chemistry.[1,2] If an organometallic Lewis acid, especially of group 3B, reacts with a Lewis base having an acidic proton, an adduct will frequently be observed before the cleavage reaction occurs under appropriate conditions.[1,2] The species eliminated by the cleavage process is a small molecule composed of a substituent originally bound to the organometallic compound and the proton from the base. This elimination reaction finds many important applications. The semiconductor gallium arsenide[3] is synthesized from $Ga(CH_3)_3$ and $AsH_3$ by a series of elimination reactions which ultimately produce 3 mol of methane. The hydrolysis of neutral organometallic compounds[1,2] and the cations which are the serious toxic pollutants of the aqueous environment[4] provide more examples of the elimination reaction. Products from the elimination reaction have also been used in the formation of a variety of polymers and polymerization catalysts.[2]

Despite the significance of the elimination reaction to group 3B chemistry, very little is known about the mechanism of the reaction.[1,2] The common observation of the formation of a Lewis acid–base adduct prior to the elimination reaction led researchers to conclude that the elimination reaction is a reaction of a preformed adduct.[1,5] The observed differences in reactivity of adducts for elimination were then rationalized by considering the effects of electrical strain in the adduct molecules.[5] For example, trimethylaluminum reacts more readily with methanol than dimethylamine to eliminate methane.[1,2] This observation has been attributed to the presence of a more acidic proton in methanol than dimethylamine.[1] It is regretable that none of these ideas have been supported or denied by kinetics or spectroscopic data. There has only been one report in the literature of a kinetics study of an elimination reaction of an aluminum, gallium, or indium compound. Gosling and Bowen[6] attempted a kinetics study of the elimination reaction of $Cl(C_2H_5)_2AlN(CH_3)_2H$ by following the rate of formation of ethane from the pyrolysis of pure adduct in the condensed phase at 110 °C. Their results did not give any information about the molecularity of the reaction or a possible mechanism.

In this paper we report the kinetics of and propose a mechanism for the elimination reaction which occurs between dimethylaluminum hydride and *N*-methylaniline in toluene solution at −63 °C. Equation 1 describes the stoichiometry

$$[(CH_3)_2AlH]_3 + 3N(C_6H_5)(CH_3)H \rightarrow {}^3/_2[(CH_3)_2AlN(C_6H_5)(CH_3)]_2 + 3H_2 \quad (1)$$

of the reaction which was studied. This reaction was chosen because the rate of reaction could be easily monitored by following the formation of hydrogen manometrically. In addition, corrections for the solubility of hydrogen in toluene would not be needed. The goal of our experiments was to determine the mechanism of the elimination reaction and the participation, if any, of a preformed adduct.

## Experimental Section

All compounds were manipulated in a vacuum line or a purified inert-gas atmosphere. Toluene was dried by refluxing over sodium. *N*-methylaniline was dried over KOH pellets and distilled just before use. Dimethylaluminum hydride[7] was prepared from $LiAlH_4$ and $Al_2(CH_3)_6$ by heating the mixture for 1 h at 80 °C. The product, which was purified by vacuum distillation, had properties in every respect identical with those previously reported for dimethylaluminum hydride.[7,8]

**Nature and Stoichiometry of the Elimination Reaction.** The stoichiometry of the elimination reaction between dimethylaluminum hydride and *N*-methylaniline was examined. When 0.1140 g (1.96 mmol) of $(CH_3)_2AlH$ was combined with 0.2100 g (1.96 mmol) of $N(C_6H_5)(CH_3)H$, 1.95 mmol of $H_2$ (measured with Toepler pump and gas buret assembly) was formed. No methane was observed as a product. Additional experiments using excess *N*-methylaniline confirmed the identical stoichiometry. When excess dimethylaluminum hydride was used, a different aluminum–nitrogen product, probably $(CH_3)_2AlN(C_6H_5)(CH_3)Al(CH_3)_2H$, was observed.[9]

The aluminum–nitrogen product of the observed reaction is a dimer,[10] $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, which exists as a mixture of cis and trans isomers. Our $^1H$ NMR measurements in toluene solution suggest that the cis isomer predominates. At room temperature the product has an 84% cis and 16% trans isomer distribution in toluene solution. A similar isomer ratio has been observed for this compound in other solvents.[10]

**Kinetics Experiments.** The apparatus for the kinetics study is shown in Figure 1. Dimethylaluminum hydride was quantitatively transferred to the apparatus by pumping a weighed sample into the cooled (−196 °C) vessel. The alane was carefully dissolved in 2.00 mL of toluene, measured by pipet, and vacuum distilled into the apparatus. The toluene solution of *N*-methylaniline was prepared in a 5.00-mL volumetric flask which had been purged with argon. For the kinetics experiment, 4.00 mL of the amine solution was pipetted into the side arm dumper, attached to the kinetics apparatus, frozen to −196 °C, and evacuated. Then, the amine and the alane solutions

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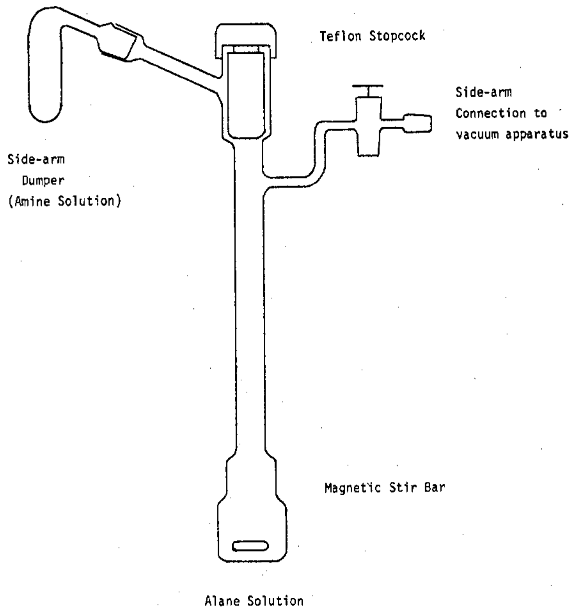


**Figure 1.** Kinetics apparatus.

were warmed to room temperature and finally cooled to −63 °C (chloroform slush bath) for 30 min prior to mixing. The short length of glassware between the solutions was cooled, the two solutions were mixed, the timer was initiated, and the pressure of the evolved hydrogen was measured as a function of time. A constant rate of stirring was maintained throughout the kinetics experiment by a magnetic stirring bar. After the last kinetics measurement, the −63 °C bath was removed and the solution was warmed to room temperature to effect complete evolution of hydrogen. Then, the volatilized toluene was condensed back into the reaction vessel by cooling the latter to −196 °C. Finally, the −63 °C bath was replaced around the apparatus. After there was no pressure change, the "infinite-time" hydrogen pressure was measured.

All experimental variables which might alter the pressure measurements were maintained as constant as possible. The volume of the reaction solution was 6.00 mL in all experiments. The change in the gas volume due to the lowering of the mercury level in the manometer never exceeded 3% of the total volume.[11] It should be noted that this factor limits the maximum quantity of dimethylaluminum hydride which could be used. The error in the $H_2$ pressure measurements was ±0.5 mm.

## Results and Discussion

The kinetics of the reaction between dimethylaluminum hydride and *N*-methylaniline in toluene solution was investigated by following the rate of evolution of hydrogen under two sets of experimental conditions: (1) equal concentrations of the alane (calculated as the concentration of the monomeric unit) and the amine and (2) pseudo-first-order conditions with an excess of the amine. Experiments using an excess of the alane are prohibited because a different final product is formed.[9] Two general conclusions can be made from our experiments. The rate of formation of hydrogen is significantly faster when the concentrations of the alane and the amine are equal than under pseudo-first-order conditions. Second, the kinetics order for the formation of hydrogen changes from second to first as conditions change from equal concentrations to pseudo-first-order. This change in kinetics order suggests an equilibrium step in the mechanism.[12]

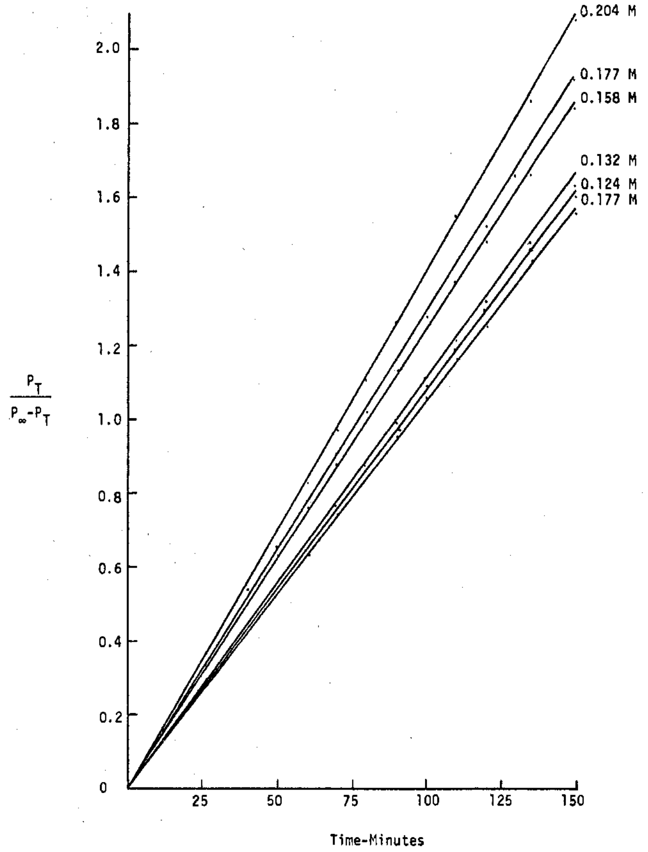


**Figure 2.** Second-order kinetics plots for equal concentrations of the alane and the amine.

**Table I.** Rate Data for Equal Concentrations of $(CH_3)_2AlH^a$ and $N(C_6H_5)(CH_3)H$

| init concn,[a] M | $k_{obsd}$,[b] $s^{-1}$ | $[(CH_3)_2AlH]_{eq}$,[c] M | $10^3k_{calcd}$,[d] $M^{-1}\,s^{-1}$ | $K_a$,[e] M |
|---|---|---|---|---|
| 0.204 | 2.33 | 0.0388 | 6.01 | 110 |
| 0.177 | 2.12 | 0.0353 | 6.01 | 114 |
| 0.158 | 2.03 | 0.0338 | 6.01 | 109 |
| 0.132 | 1.78 | 0.0296 | 6.01 | 116 |
| 0.124 | 1.77 | 0.0294 | 6.02 | 113 |
| 0.117 | 1.72 | 0.0286 | 6.01 | 105 |

[a] Concentrations of $(CH_3)_2AlH$ are based on the number of moles of the monomeric unit. [b] $= k[(CH_3)_2AlH]_{eq} \times 10^4$. The value given is the slope (least squares) of $P_T/(P_\infty - P_T)$ vs. time plot. The standard deviation of the slope was $0.01 \times 10^{-4}$ in all cases. All lines had a correlation factor greater than 0.999. [c] Calculated by using pseudo-first-order kinetics data, $k_{obsd} = k/K_a$ and assuming a value of $K_a = 110$. See Results and Discussion. [d] Calculated by dividing $k_{obsd}$ (column 2) by $[(CH_3)_2AlH]_{eq}$ (column 3). [e] Calculated by using the mass action expression for the equilibrium

$$H(CH_3)_2Al + N(C_6H_5)(CH_3)H \overset{K_a}{\rightleftharpoons} H(CH_3)_2AlN(C_6H_5)(CH_3)H$$

When the concentrations of the alane and the amine are equal, the elimination of hydrogen follows second-order kinetics, as shown by the linearity of the kinetic plots[13] of $P_T/(P_\infty - P_T)$ vs. time (Figure 2). These reactions were followed for 150 min (61–67% completion). The kinetics data from these plots are summarized in Table I. It is apparent that the data do not fit a second-order rate law based on initial concentrations. If the values of $k_{obsd}$ from the slopes of the second-order kinetics plots are divided by the initial concentration of either the alane or the amine,[13] a constant value for the rate constant is not obtained. However, a constant value can be calculated by dividing $k_{obsd}$ by the appropriate equilibrium concentration of the monomeric alane or amine (see following discussion).

When the kinetics of the reaction are observed under pseudo-first-order conditions (excess amine), hydrogen is eliminated in a first-order process. The pseudo-first-order kinetics plots of log $(P_\infty - P_T)$ vs. time had no deviations over a period of 2 half-lives, approximately 450 min. The kinetics data are summarized in Table II. The major conclusion from these data is the observed pseudo-first-order rate constants are

**Table II.** Rate Data Obtained under Pseudo-First-Order Conditions with Excess $N(C_6H_5)(CH_3)H$

| $[N(C_6H_5)(CH_3)H]$, M | $[(CH_3)_2AlH]$,[a] M | $10^5 k_{obsd}$, $s^{-1}$ | $r^2$ [b] |
|---|---|---|---|
| 2.51 | 0.207 | 5.12 ± 0.01 | 0.999 928 |
| 2.33 | 0.204 | 5.03 ± 0.01 | 0.999 618 |
| 2.20 | 0.0862 | 5.82 ± 0.04 | 0.998 952 |
| 2.20 | 0.123 | 5.47 ± 0.01 | 0.999 725 |
| 1.44 | 0.138 | 5.87 ± 0.05 | 0.998 108 |
| 1.34 | 0.102 | 5.42 ± 0.03 | 0.999 158 |
| | | 5.46 av | |

[a] Concentrations of $(CH_3)_2AlH$ are based on the number of moles of the monomeric unit. [b] Least-squares correlation value.

independent of the amine concentrations in the range studied.

Equations 2–5 can be used to explain all of our kinetic data

$$[(CH_3)_2AlH]_3 \rightarrow 3(CH_3)_2AlH \quad (2)$$

$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \overset{K_a}{\rightleftharpoons} H(CH_3)_2AlN(C_6H_5)(CH_3)H \quad (3)$$

$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3) \quad (4)$$

$$2(CH_3)_2AlN(C_6H_5)(CH_3) \rightarrow [(CH_3)_2AlN(C_6H_5)(CH_3)]_2 \quad (5)$$

and are consistent with the chemistry of the system. The only assumption which must be made for this mechanism is that the initial formation of adduct is extremely rapid. This assumption is consistent with this Lewis acid–base chemistry,[1,2] other kinetics studies of aluminum hydrides,[14,15] and related low-temperature $^1H$ NMR observations.[9] The rate law for this mechanism is given by expression 6. The terms

$$\frac{dP_{H_2}}{dt} = \frac{-d[(CH_3)_2AlH]_T}{dt} = \left\{\frac{k}{1 + K_a[N(C_6H_5)(CH_3)H]_T}\right\}[(CH_3)_2AlH]_T \times [N(C_6H_5)(CH_3)H]_T \quad (6)$$

calculated kinetic constants

$$k = 6.01 \times 10^{-3}\ M^{-1}\ s^{-1}$$

$$K_a = 110\ M^{-1}$$

$[(CH_3)_2AlH]_T$ and $[N(C_6H_5)(CH_3)H]_T$ express the total dimethylaluminum hydride and *N*-methylaniline concentrations before elimination. Under the pseudo-first-order conditions, the observed rate constant ($k_{obsd}$) is independent of the amine concentration. If $K_a$ is sufficiently large, $k_{obsd}$ equals $k/K_a$, according to our rate law. However, when the concentrations of the alane and the amine are equal, the rate of formation of hydrogen shows second-order kinetics, which is consistent with eq 4. The slope of the second-order kinetics plot[13] is given by $k[(CH_3)_2AlH]_{eq}$ or $k[N(C_6H_5)(CH_3)H]_{eq}$, where $[(CH_3)_2AlH]_{eq}$ and $[N(C_6H_5)(CH_3)H]_{eq}$ are the equilibrium concentrations. Numerical values for both the second-order rate constant, $k$, and the equilibrium concentrations are unknown. However, if the substitution $k = k_{obsd}K_a$, from the pseudo-first-order data, is made and $K_a$ is estimated, equilibrium concentrations of the alane or the amine can be calculated. Knowledge of the initial and calculated equilibrium concentrations permit a recalculation of $K_a$ with the mass action expression. After a series of successive approximations, the values of the assumed and calculated equilibrium constant, $K_a$, agreed (Table I). The results of these calculations support the proposed mechanism.

The other mechanism (eq 7 and 8) which must be considered is given by the two kinetically important steps (7) and (8). These two steps replace eq 3 and 4. The other steps remain the same. Equations 7 and 8 are kinetically similar

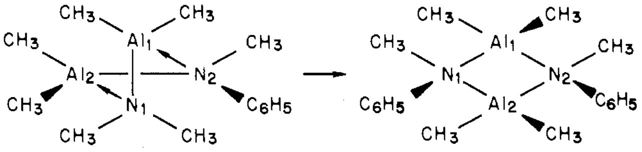
$$(CH_3)_2AlH + N(C_6H_5)(CH_3)H \overset{K}{\rightleftharpoons} H(CH_3)_2AlN(C_6H_5)(CH_3)H \quad (7)$$

$$H(CH_3)_2AlN(C_6H_5)(CH_3)H \xrightarrow{k} H_2 + (CH_3)_2AlN(C_6H_5)(CH_3) \quad (8)$$

to the preferred mechanism (eq 2–5) but involves the elimination of hydrogen from the adduct. However, our data are not consistent with eq 7 and 8. If this scheme was appropriate and $K$ was large, hydrogen should be formed in a first-order elimination reaction. Such observations were made under pseudo-first-order conditions but not when the alane and the amine concentrations were equal. Furthermore, if the adduct was the species which eliminated hydrogen, the excess amine present in the pseudo-first-order experiments should have increased the rate of elimination, when compared to the rate observed for equal concentrations of the amine and the alane, rather than the observed decrease. In the preferred mechanism (eq 2–5), the excess amine increases the concentration of adduct but decreases the concentration of the other reactive species, the monomeric alane.

The major conclusion from our kinetics study is that elimination is a second-order reaction between a monomeric alane species and the amine. Hydrogen is not eliminated from the adduct in this particular system. Our results clearly show that adduct formation is a "dead-end" path for the elimination reaction. The preferred mechanism (eq 2–5) suggests that the adduct dissociates into the monomeric alane and the amine, probably within a solvent shell. If the alane and the amine then recombine with the appopiate orientation, elimination occurs, possibly by a four-centered $S_Ei$ process.[16] The concept of dissociation and reaction within a solvent shell is consistent with the chemistry of organoaluminum compounds in aromatic solvents,[17–19] but we have no specific data which support or deny it for our system.

The final product from the elimination reaction is an aluminum–nitrogen dimer $[(CH_3)_2AlN(C_6H_5)(CH_3)]_2$, which exists as a 4:1 mixture of cis/trans geometrical isomers. This isomer ratio is not a function of solvent polarity.[10] Since the trans isomer is most favored by thermodynamic effects, kinetic factors could be responsible for the observed predominance of the cis isomer. The product distribution might be controlled by the relative energies of the transition states for the formation of the two isomers. If the dimerization reaction is a cycloaddition reaction between two aluminum–nitrogen species with partial $\pi$ bonding, the cis isomer can be the preferred product. The orthogonal approach of the $\pi$ bonds of two monomeric units in the least hindered orientation, followed by a $_2\pi_s + _2\pi_a$ cycloaddition[20] (eq 9), could result in selective cis dimer formation. The favored transition state minimizes the interactions between the most bulky substituents, the phenyl groups. This cycloaddition rationale also is consistent with the observed absence of major solvent polarity effects[10] on the cis/trans ratio. A similar cycloaddition process[21] has been used to explain the selective cis olefin formation in a Wittig reaction



preferred transition state favored cis isomer

(9)

between a phosphorus ylide and an aldehyde. It is of interest to speculate that the proposed cycloaddition reaction precludes the formation of higher polymeric aluminum–nitrogen species from the observed elimination reaction.

Our kinetics data suggest that the major factors which influence the rate of elimination will be those which alter the equilibrium constant for adduct formation, $K_a$, and the second-order rate constant, $k$. More kinetics studies will be required to elucidate the mechanism of elimination for other Lewis acid–base systems and to distinguish the relative importance of the effects of $K_a$ and $k$ when identical mechanisms are involved. We are also investigating the effects of substituents and the nature of the base atom on the steric course of the proposed cycloaddition reaction.

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**Registry No.** $H(CH_3)_2Al$, 865-37-2; $N(C_6H_5)(CH_3)H$, 100-61-8; *cis*-$(CH_3)_2AlN(C_6H_5)(CH_3)$, 56649-31-1; *trans*-$(CH_3)_2AlN(C_6H_5)(CH_3)$, 56604-60-5.

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# Kinetics of Reduction of Cobalt(III)–Ammine Complexes by Dithionite

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The kinetics of reduction of several pentaamminecobalt(III) complexes by dithionite have been studied. The observed pseudo-first-order rate constant has the general form $k = k'[S_2O_4^{2-}]^{1/2} + k''[S_2O_4^{2-}]$ which is common for dithionite reductions. The pyridine and ammonia complexes show only the $k'$ term, and this is assigned to an outer-sphere mechanism for these as well as for the sulfato and chloro complexes. This assignment is consistent with comparisons to reductions by $Ru(NH_3)_6^{2+}$. The later comparisons also indicate that the $k''$ path occurs by a "bridging" mechanism for the azido, sulfato, trichloroacetato, and benzoato complexes. It is proposed that the ratio $k'/k_{Ru}$ may be used to determine oxidant charge since the two reductants have opposite charges and respond in opposite ways to changing oxidant charge.

## Introduction

Dithionite is widely used as a reducing agent, especially in in vitro biological systems under neutral or alkaline conditions. Kinetic studies on dithionite reductions[1-12] indicate that mechanism 1 is generally applicable, where Ox is the oxidizing agent.

$$S_2O_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2SO_2^- \quad K_1 = k_1/k_{-1} \tag{1a}$$

$$Ox + S_2O_4^{2-} \xrightarrow{k_2} product \tag{1b}$$

$$Ox + SO_2^- \xrightarrow{k_3} product \tag{1c}$$

The reactions considered here all involve metal-ion reduction, and three mechanistic possibilities are usually recognized. These are (i) outer-sphere electron transfer, perhaps through a porphyrin ligand if present, (ii) inner-sphere electron transfer which occurs subsequent to substitution for one ligand by the reducing agent $SO_2^-$ or $S_2O_4^{2-}$, and (iii) a bridging mechanism in which the reducing agent forms an adduct with a coordinated ligand prior to electron transfer. The second mechanism has been eliminated in several systems[6,12] because ligand substitution was known to be much slower than electron transfer and the reduction product with the original ligand system intact could be identified.[4,12] The observations have been used to infer an outer-sphere mechanism, but, in fact, this does not eliminate a bridging mechanism, as pointed out by James and Hambright[2] and, more recently, by Eaton and Wilkins.[11]

The effect of various ligands coordinated to the metal has been explored in several cases but most extensively, with metmyoglobin as an oxidant, by Wilkins and co-workers[9,11] and by Cox and Hollaway.[10] Most systems have been studied with $H_2O$, $OH^-$, pyridine, and $CN^-$ ligands, and the relative rates of dithionite reduction vary with the oxidant. For example, the order of rates with a manganese(III) porphyrin[2] is py > $OH^-$ > $H_2O$, with a cobalt(III) porphyrin[6] $(OH_2)_2 \gg (OH_2)(OH^-) > (py)_2$, with hemin[8] $(py)_2 \gg (OH_2)_2 \gg (OH_2)(OH^-)$, and with horse heart metmyoglobin[11] py $\gg OH_2 > CN^- \gg OH^-$. These limited observations indicate that the relative rates depend on the metal ion being reduced. The results have been rationalized on the basis of relative reactant, product stability, and ligand rearrangement requirements.[6,8,12] Most recently Wilkins and co-workers[9,11] have proposed a nucleophilic attack of $SO_2^-$ on pyridine and imidazole to explain the high reduction rates when these ligands are coordinated to horse heart metmyoglobin. This proposal was shown to be consistent with the kinetic effects of substitution on the ligand.

The systems studied thus far have the attraction of biological implication but have the concomitant property of complexity. In the hope of clarifying some of the mechanistic details of dithionite reductions this study of the reductions of pentaamminecobalt(III) complexes was undertaken. These complexes are kinetically inert and have been studied with a wide